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Summary of Airborne Chlorine and Hydrogen Chloride
Gas Measurements for August 20 and September 5, 1977
Voyager Launches at Air Force Eastern Test Range,
Florida

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SUMMARY OF AIRBORNE CHLORINE AND HYDROGEN CHLORIDE GAS MEASUREMENTS
FOR AUGUST 20 AND SEPTEMBER 5, 1977 VOYAGER LAUNCHES AT AIR FORCE
EASTERN TEST RANGE, FLORIDA

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SUMMARY

This report summarizes airborne chlorine and hydrogen chloride gas measurements made following the Voyager launches of August 20 and September 5, 1977. Launch was at 1029 EDT (August 20) and 0856 EDT (September 5) from Launch Complex 41 at the Eastern Test Range, Florida. As part of NASA's ongoing tropospheric research program on the effects of launch vehicle exhaust emissions on tropospheric air quality, airborne effluent measurements were made, in situ, in the stabilized ground cloud. Measurements were made from about 2 minutes after launch to as long as 4-1/2 hours after launch in the case of the September launch. All sampling was in an altitude range of about 700 to 1500 meters at distances out to 100 km from the launch pad.

The maximum observed hydrogen chloride concentration for both launches was about 25 to 30 ppm occurring typically 2 to 6 minutes after launch. By completion of the sampling missions (1-1/2 hours for August and 4-1/2 hours for September), the maximum in-cloud concentration was observed to be about 1 to 2 ppm. Maximum observed chlorine concentrations were about 40 to 55 ppb at about 2 to 8 minutes after launch. By about 15 minutes after launch, this concentration decreased to less than 10 ppb (lower detection limit of instrument). The in-cloud chlorine concentration was well below 1 percent of the hydrogen chloride concentration, and generally of the order of a few tenths of a percent of the in-cloud hydrogen chloride concentration. The measurement data support the theory of low in-cloud chlorine concentrations as compared to hydrogen chloride as developed from earlier thermochemical calculations. The appendix of the report discusses the chlorine instrument and the results of laboratory evaluation of the detector and sampling procedures.

INTRODUCTION

The National Aeronautics and Space Administration (NASA) is actively pursuing tropospheric and stratospheric environmental studies in conjunction with the launch and operation of rocket vehicles. One major portion of the tropospheric program is directed toward measuring

and predicting the impact of rocket exhaust effluents produced at launch on the surface level air quality. Since 1972, the Langley Research Center has been conducting a launch vehicle effluent (LVE) monitoring program (refs. 1-6) at the Air Force Eastern Test Range, Florida, using regularly scheduled launch vehicles (primarily Titan III) as targets-of-opportunity. The goal of the LVE program is to assess the applicability and accuracy of diffusion models for predicting the dispersion of exhaust effluents from current and future launch vehicles used by NASA. The approach employed to meet these objectives is the measurement of rocket products produced by the launch of large solid rocket motor launch vehicles. Measurements are made both at surface level and within the "stabilized ground cloud" formed in the troposphere as the result of the launch. These measurements are then compared with the various analytical schemes (refs. 7-9) for predicting the exhaust effluent concentrations.

The initial phase of the LVE program was directed toward measurements of the major species, hydrogen chloride gas and aluminum oxide particulates, found in the launch cloud. Other measurements were directed toward the verification of important inputs required by the models for predicting the surface level effluent concentrations. The measurements discussed herein are directed toward chlorine, one of the less abundant species found in the launch cloud. The initial calculations (ref. 10) of the composition of the exhaust products for the launch cloud were focused only on the composition of the exhaust at the exit plane (nozzle throat) of the rocket motor, and did not include plume afterburning or chemical reactions in the plume wake. Subsequent calculations which included plume afterburning (ref. 11) showed a conversion of some of the hydrogen chloride to chlorine gas. These calculations showed that about 2 percent of the afterburned rocket exhaust is chlorine gas and that Cl_2 concentrations are approximately 10 percent of the HCl concentrations. By the time the stabilized ground cloud has formed (T+5 to T+15 minutes), this afterburned exhaust is greatly diluted by ambient air entrainment (less than 1 percent of the stabilized cloud mass is exhaust products). As a result of the expected low chlorine concentrations, the measurement program is directed toward airborne measurements in the cloud rather than surface-level measurements beneath the cloud. The sampling mission was directed at (1) defining the chlorine concentrations in the stabilized cloud, and (2) measuring the ratio of chlorine to hydrogen chloride in the cloud. The aircraft used in the sampling mission was equipped to monitor HCl , Cl_2 , NO , NO_x , particulates, some meteorological parameters, and position data for the aircraft. In addition, ground base infrared and visible photography of the physical characteristics and behavior of the cloud were conducted. This report discusses only the HCl and Cl_2 measurements; reference to the other measurements are made only as required for documentation or explanation of the HCl and Cl_2 data.

SYMBOLS

EDT	-	Eastern Daylight Time
LVE	-	Launch Vehicle Effluent
NASA	-	National Aeronautics and Space Administration
ppb	-	Parts-per-billion by volume
ppm	-	Parts-per-million by volume
T	-	Time after launch
UT	-	Universal Time

PROGRAM DESCRIPTION

Launch Vehicle and Exhaust Cloud Formation

The chlorine measurement program was conducted in association with two Titan III launches at the Air Force Eastern Test Range, Florida, August 20, and September 5, 1977. Both launches were from Launch Complex 41. Launch times were 1029 EDT (1429 UT) and 0856 EDT (1256 UT) for the August and September launches, respectively.

The Titan III launch vehicle and propulsion systems are discussed in references 5 and 6. At lift-off, only the Titan III solid rocket motor boosters are ignited. The other Titan propulsion systems are ignited at altitude and do not contribute effluents to the ground cloud. Depending upon meteorological conditions, the first 10 to 20 seconds of solid rocket motor booster exhaust contribute effluents to the cloud. The two solid rocket booster motors have a combined and nearly constant mass flow rate of about 4×10^6 grams per second during these first 20 seconds. Table I shows the exhaust product composition following plume afterburning. In addition, the table shows nominal in-cloud (5 to 10 minutes after launch) concentration levels for those constituents measured during earlier LVE monitoring programs (refs. 1-6).

A description of a typical stabilized ground cloud is found in references 5 and 6. The cloud usually stabilizes 5 to 15 minutes after launch at several kilometers from the launch site, has a centroid (cloud) stabilization altitude of 500 to 3000 meters, and a stabilization volume of 2 to 10 cubic kilometers. Under favorable meteorological conditions, the stabilized ground cloud may be visible for at least 1 hour after the launch and be transported 20 to 30 kilometers from the launch pad during this time. The physics of cloud formation is highly dependent on the prevailing meteorological and thermodynamic properties of the troposphere.

Airborne Instrumentation and Sampling Plan

The airborne sampling platform (twin engine, light aircraft) is described in detail in reference 12. Characteristics of the sampling instrumentation are also found in reference 12. References 1, 13, and 14 provide additional background information on the types of instrumentation used. The HCl detector is based on a chemiluminescent reaction in which visible light is generated in an alkaline solution of luminol during oxidation by hydrogen peroxide. Figure 1 is a diagram showing the operating principle. The instrument contains a reaction cell from which the visible light is monitored by a photomultiplier tube. The output light from the cell is proportional to the HCl concentration of the incoming sample stream. Prior to reaching the reaction cell, the incoming airstream passes through an alumina tube coated with sodium bromate and sodium bromide. This coating reacts with the HCl to produce bromine which is a catalyst for the luminol oxidation (chemiluminescent process). The chemiluminescent process is equally sensitive to chlorine gas; however, the Cl_2 concentrations encountered in the cloud are insignificant compared to HCl levels and the 15 or 20 percent accuracy of the HCl measurement. Thus, no attempt was made to correct the HCl instrument output for chlorine interference. For airborne applications of the instrument, the coated inlet tube extends forward of the nose of the aircraft to sample undisturbed free-stream air. Table II shows the detection characteristics of the HCl detector.

The chlorine detector used is a modification of the HCl detector. The instrument operates similarly to that of the HCl detector but with two differences. First, the chlorine instrument uses only luminol in the reaction cell. The hydrogen peroxide stream is replaced with a second luminol stream. This decreases the sensitivity of the instrument to HCl. Secondly, the bromate-bromide coated inlet tube of the HCl detector is replaced with an inlet system consisting of a teflon inlet tube and a glass wool filter which selectively removes HCl without affecting chlorine. The laboratory evaluation of the chlorine instrument for detecting Cl_2 gas is discussed in detail in the appendix. Table II also summarizes the detection capabilities of the Cl_2 instrument. Air sampled forward of the aircraft nose is ducted approximately 6 meters to the instrument located in the aft passenger cabin. As shown in the appendix, this is a valid sampling technique for chlorine gas.

The airborne sampling plan is described in some detail in reference 12. The sampling plan is designed to sample the launch cloud as early as 2 minutes after launch. Sampling continues until the cloud cannot be identified from the ambient background or until about $T + 1\frac{1}{2}$ hours at which time the aircraft must land for refueling. Alternate sampling plans have been developed for those cases when the aircraft crew loses contact with the cloud due to early dispersion of the cloud or poor visibility (weather). Table III gives the time and altitude for each sampling pass conducted during the launches. The time shown for each

pass corresponds to the approximate point at which maximum HCl was sensed during each pass. Sampling altitude was taken from the aircraft altimeter recorded manually during the flights. For the August launch, approximately 30 sampling passes were made from about T+12 minutes to T+100 minutes, covering an altitude range of 700 meters to 1400 meters. For the September launch, approximately 50 passes were made from about T+2 minutes to T + 4-1/2 hours, and for an altitude range of 700 meters to 1500 meters. For the September launch, the aircraft landed, after pass 28, refueled, and made a second series of flights through the cloud for passes 29 through 50.

RESULTS AND DISCUSSION

As discussed earlier, during the August 20 launch, 30 sampling passes of the cloud were made from about 2 to 100 minutes after launch. Figure 2 shows the HCl and Cl₂ data for the first 6 passes. Beyond pass 6, Cl₂ concentrations were below the 10 ppb detection limit of the instrument. As a result of a procedural error, the chlorine detector malfunctioned during the first pass and no chlorine data were obtained. Shown for each pass is the T-time corresponding to zero seconds on the data plots. This time is expressed in minutes:seconds after launch. HCl data were obtained for all 30 passes and by about T+10 minutes (pass 30) had declined to about 1 to 2 ppm. Figure 3 shows similar data for the September 5 launch. Approximately 50 sampling passes of the cloud were made from 2 minutes to 4.5 hours after launch. Chlorine concentrations after pass 6 were 10 ppb or less. By approximately 4 hours after launch, HCl in the cloud had decayed to about 1 ppm.

The following points are noted from figures 2 and 3.

1. Generally the Cl₂ concentrations encountered were lower than the lowest calibration point (50 ppb) considered in the laboratory study of the detector. It is believed that the instrument's calibration can be linearly extrapolated to below 10 ppb Cl₂ with little additional uncertainty. The Cl₂ detection limit was conservatively estimated at 10 ppb based on signal-to-noise, but is probably lower. Laboratory studies with the similar HCl detector shows its calibration to be linear from 5 ppb to 50 ppm HCl.
2. The in-cloud concentration as a function of time was similar for both HCl and Cl₂. This is consistent with earlier measurements of the gaseous species (ref. 5 and 6) showing similar in-cloud concentration time variations for HCl and NO/NO_x.

3. For the August launch, the HCl filter was not 100 percent effective in removing HCl from the Cl₂ sampling line. The Cl₂ peaks for sampling passes 3 through 6 (fig. 2) are the result of both the Cl₂ concentration in the cloud and a small amount of HCl leakage through the filter. Chlorine peak concentrations for these passes are probably of the order of 20 to 55 ppb rather than the 60 to 80 ppb shown. Complete HCl filter breakthrough as described in the appendix never occurred for the August launch; instead, the HCl leakage through the filter increased with subsequent sampling passes. For the September launch, the filter behavior was as observed in the laboratory, showing little HCl leakage through the filter and complete filter breakthrough by about pass 20.
4. No correction has been applied to the data to correct for sampling line delay times associated with the two measurements. The HCl data lead the Cl₂ data by approximately 10 seconds which is consistent with the HCl instrument location in the aircraft nose and the Cl₂ instrument location in the aft passenger cabin.

Table IV shows a comparison of the maximum HCl and Cl₂ concentration observed for each sampling pass of figure 2 and 3. For the August launch, passes 3 through 6, two maximum Cl₂ concentrations are shown. The primary value is that from figure 2; the other value shown in parenthesis indicates what is thought to be the true maximum Cl₂ concentration after allowing for HCl leakage through the filter. The ratio of maximum Cl₂ to maximum HCl concentration for each pass is also shown. This ratio ranges from about 6×10^{-4} to 9×10^{-3} indicating that the Cl₂ concentration is about 0.06 to 0.9 percent of the in-cloud HCl concentration. Because of the low level of Cl₂ concentrations measured, the HCl filter leakage problem for the August launch, and the fact the laboratory calibrations were not conducted below 50 ppb Cl₂, it is difficult to determine this exact ratio; however, the data clearly indicate that Cl₂ concentrations in the cloud are well below 1 percent of the HCl concentrations and most likely of the order of a few tenths of a percent of the HCl. While these data indicated that the Cl₂ concentrations are lower than 10 percent of the HCl concentration (2 percent of total exhaust) calculated from thermochemical consideration, there is agreement that Cl₂ is a very minor specie in the LVE cloud and of little consequence in its effect on ambient air quality. The HCl concentrations shown in table IV are comparable to those of earlier launches (ref. 4), thus indicating that the effluent concentrations measured for these Titan launches are in general representative for Titan III launch clouds.

CONCLUSIONS

Based on the data from the two Titan III launches the following conclusions concerning HCl and chlorine gas in the stabilized ground cloud apply:

1. Maximum hydrogen chloride concentrations for both launches were about 25 to 30 ppm occurring 2 to 6 minutes after launch and decayed to 1 to 2 ppm by 1-1/2 and 4-1/2 hours after launch for the August and September launches, respectively.
2. Maximum chlorine concentrations were about 40 to 55 ppb and decayed to less than 10 ppb by about 15 minutes after launch.
3. Maximum in-cloud chlorine concentrations were well below 1 percent of the maximum hydrogen chloride concentrations, and probably as low as a few tenths of 1 percent.
4. The measurement data agree with earlier thermochemical calculations which suggest that chlorine gas is not present in sufficient quantity to be environmentally significant.
5. The HCl concentrations measured for these Titan III launches were comparable with those of earlier Titan III launches indicating that the Cl_2 concentrations reported here are representative for Titan III launch clouds in general.

APPENDIX

SUMMARY OF LABORATORY EVALUATION OF

AIRBORNE CHLORINE INSTRUMENT AND SAMPLING PROCEDURES

The airborne chlorine (Cl_2) detector is a modified version of a hydrogen chloride detector which has been used for several years to monitor surface level hydrogen chloride (HCl) gas concentrations in the NASA Launch Vehicle Effluent (LVE) monitoring program conducted by the Langley Research Center. A photograph of the HCl detector is shown in figure 4. The operational characteristics of the basic, unmodified instrument are discussed in detail in references 13 and 15. Three minor modifications were made to the HCl detector to convert the unit to chlorine sensing. Since the basic HCl detector is equally sensitive to both hydrogen chloride and chlorine gas, all three modifications were designed to desensitize the detector response to HCl. This appendix will describe the results of the laboratory program conducted to verify these modifications, the measurement capabilities

of the modified detector for Cl_2 , and the airborne operational procedures used in making the LVE Cl_2 measurements.

Chlorine Detection Requirements

Results from previous LVE monitoring activities show that for the Titan III launch vehicle, in-cloud HCl concentrations range from about 5 to 40 ppm several minutes after launch, to less than 0.5 ppm about 1 hour after launch. Aircraft residence time in the effluent cloud is about 10 to 30 seconds at a flight speed of 50 m/s. Based on this information and thermochemical calculations that in-cloud Cl_2 concentrations are about 5 to 10 percent, by volume, of the HCl concentration (2 percent by mass of total afterburned exhaust products), the design parameters for the airborne Cl_2 detector were as follows:

1. Detection range of 50 ppb to 10 ppm.
2. Negligible interference from HCl in concentrations of up to 10 ppm.
3. Response time of about 2 seconds to achieve 90 percent of reading.

The laboratory studies were conducted for purposes of developing and certifying an airborne Cl_2 measurement system (hardware and procedures) capable of the above measurement parameters.

Instrument Modifications

Figure 1 is a schematic of the basic HCl detector. The reader is referred to reference 13 for a discussion of the theory of detection. With reference to figure 1, the first modification was to replace the bromide-bromate coated alumina inlet tube with a non-coated flexible teflon tube. The basis of the instrument as a HCl detector is the reaction of HCl with the bromide and bromate to produce Br_2 as well as additional bromine and chlorine compounds which react with luminol and peroxide in the reaction cell to cause chemiluminescence. Light output from this reaction is proportional to the HCl concentration in the air sample. Thus, elimination of the coated inlet tube prevents the formation of Br_2 and desensitizes the instrument to HCl. However, Cl_2 is about as efficient as Br_2 in the chemiluminescent reaction, and little effect on instrument sensitivity to Cl_2 occurs.

The second modification was to eliminate the use of hydrogen peroxide reagent in the chemiluminescent reaction. This was done by simply replacing the peroxide reagent reservoir with a luminol reservoir, thus, resulting in two luminol flow streams into the reaction cell. This modification reduced the sensitivity of the instrument to both HCl and

Cl₂ but with the HCl reduction being greater. With these two modifications, the instrument was approximately five times more sensitive to Cl₂ than HCl; however, since the expected Cl₂ in-cloud concentrations were 10 to 50 times less than the HCl concentrations, a third modification was necessary.

The third modification consisted of placing an external HCl filter in the inlet line of the instrument. The purpose of the filter was to trap HCl in the incoming air sample ahead of the Cl₂ detector. As shown by the data of the appendix, with these three modifications the detector was relatively insensitive to HCl concentrations of 10 ppm while sensitive to Cl₂ concentrations as low as 50 ppb.

Sub-System Verification Tests

Sensor Calibration Test.— This phase of the laboratory studies dealt with the calibration and detection characteristics of the basic Cl₂ sensor. The basic Cl₂ sensor is defined as the modified HCl instrument minus the HCl filter. Tests consisted of introducing Cl₂-air mixtures from about 50 ppb to 10 ppm Cl₂ into the detector and recording its response. Test mixtures were prepared using a gas dilution system and the resulting mixtures were Cl₂ in air at about 50 to 70 percent humidity. Figures 5 and 6 illustrate the response of the sensor during these tests. As shown in figure 5, the instrument output was linear from 50 ppb to about 5 ppm. The calibration point at 10 ppm was rechecked numerous times (different Cl₂ gas source). No explanation is given for the non-linearity above 5 ppm, and no further laboratory investigation of the instrument's linearity was conducted. The broken lines in figure 5 represent the uncertainty in the Cl₂ gas mixtures used in the calibration, and all data points (except 10 ppm) fall within the uncertainty band of ± 20 percent. As shown in figure 6, the response time and repeatability of a given measurement was quite good.

HCl Filter Verification Test.— The next phase of the laboratory study was to characterize a suitable HCl filter. The filter found effective was a glass tube (50 cm by 5 mm internal diameter) packed with glass wool. The quantity of glass wool was not critical as long as the entire tube was filled with the wool and the packing density allowed a sample flowrate of 2 liters/minute. Preliminary tests showed that the filter required Cl₂ passivation (to eliminate loss of Cl₂ in the sample), and that the filter had a finite trapping capacity (based on HCl dosage) for HCl. A test sequence, simulating a typical airborne sampling mission, was performed in the laboratory to verify the final filter performance. The test sequence was as follows:

Step 1 - 5-minute passivation of the filter at 3 ppm Cl_2 in air at a flowrate of 2 liters/minute.

Step 2 - 1-hour purge of the filter with air at 2 liters/minute.

Step 3 - Repetitive cycles of 1-minute exposure of the filter to Cl_2 -HCl-air mixture followed by 3-minute purge with air, all at 2 liters/minute. The output of the Cl_2 detector was continually monitored during step 3.

Step 1 simulated the Cl_2 passivation of the filter in the field prior to aircraft takeoff. Step 2 simulated that time between aircraft takeoff and the first Cl_2 sampling pass of the LVE cloud. Step 3 simulated aircraft penetrations in and out of the LVE cloud. Typically 15 to 20 cloud sampling passes are made during a mission, after which the aircraft must refuel. The three-step test sequence was repeated several times at two gas concentration mixtures: mixture A - 0.2 ppm Cl_2 , 10 ppm HCl, balance air; mixture B - 1.8 ppm Cl_2 , 10 ppm HCl, balance air. New filters were used at the start of each sequence. Figure 7 shows the experimental setup. The previously mentioned gas dilution system was the Cl_2 gas source, and the HCl source was premixed HCl gas cylinders (certified before and after each test sequence). Figures 8 and 9 illustrate the response of the Cl_2 detector during step 3 of the test sequences. The zero cycle (see figures) shows the detector response to Cl_2 concentrations only (no HCl or filter). As shown in figure 8, for mixture A (0.2 ppm Cl_2 , 10 ppm HCl), the instrument output during the first cycle reached only 0.14 ppm Cl_2 indicating some Cl_2 was being trapped in the filter. This is the result of depassivation of the filter during the 1-hour purge with air. However, this is only a 30 percent loss and by the second or third cycle, the output has attained its equilibrium (same as 20th cycle) of about 0.18 ppm (only a 10 percent Cl_2 loss). On the 20th cycle, HCl breakthrough (high peak) is observed and the filter is no longer an effective HCl trap. By the completion of the 19th cycle, the filter has trapped HCl equivalent to about a 11,000 ppm-sec dosage, a quantity much higher than that from 20 passes through the LVE cloud. Figure 9 shows similar results for mixture B (1.8 ppm Cl_2 , 10 ppm HCl). The output during the first cycle is about 1.5 ppm (17 percent loss of Cl_2), but the 3rd cycle output is 1.8 ppm indicating no loss of Cl_2 . For this filter, HCl breakthrough occurs on the 29th cycle after a HCl dosage exposure of about 16,000 ppm-sec. Based on these test results, the filter is effective in trapping HCl for dosages of at least 10,000 ppm-sec. When properly passivated, the filter has minimal effect on Cl_2 concentrations (only a 10 percent loss of Cl_2) and even when depassivated by a 1-hour purge with air, only a 30 percent loss of Cl_2 was observed,

One additional test sequence was conducted with the simulated sampling system of figure 7. The purpose was to evaluate the response of the Cl_2 instrument and filter to a changing Cl_2 concentration at the aircraft

inlet probe. No HCl gas mixtures were used for these tests. The Cl_2 sampling system (aircraft lines, instrument sample lines, and HCl filter) was passivated for 5 minutes with 3 ppm Cl_2 in air and then purged with air for 10 minutes prior to the test; all at aircraft sampling flowrates. Immediately after the air purge, a Cl_2 - air mixture of approximately 0.1 to 0.15 ppm Cl_2 was introduced into the aircraft inlet probe for about 1 minute. At the end of the minute, the concentration was increased by approximately 0.1 to 0.15 ppm and was subsequently increased every minute in increments of 0.1 to 0.15 ppm until 0.5 ppm was reached. At this point, the Cl_2 concentration was decreased every minute by 0.1 to 0.15 ppm increments until 0 ppm. Figure 10 shows the results from this step change concentration sequence, and probably best indicates the overall performance of the aircraft Cl_2 sampling system.

Interference studies were conducted for nitric oxide, the only gaseous species (besides HCl) present to any extent in the LVE cloud and known to be an interferent for the chemiluminescent detector. A 5 ppm NO - air mixture (LVE cloud NO concentrations are generally well below 1 ppm) introduced through the filter into the Cl_2 sensor resulted in no output response. Liquid HCl aerosol tests with the HCl filter showed the filter an effective aerosol trap. Based on the physical characteristics of the filter, particulates should also be effectively trapped. No trapping efficiency tests were performed for particulates.

Integrated Sampling System Verification Tests

The next phase of the laboratory test program was to assemble the actual aircraft Cl_2 sampling system to verify the integrated system performance and planned operational procedures. The approach taken was to simulate, in the laboratory, actual aircraft LVE sampling sequences, procedures, effluent concentrations, and other important sampling parameters. Figure 11 is a sketch of the test setup. The aircraft inlet probe, sample transfer lines, and Cl_2 detector were actual aircraft hardware. The HCl and Cl_2 sources were those previously discussed. The simulated mission sequences used for the test were similar to those used for the filter verification tests except the 1-hour purge cycle (step 2) was replaced by a 10-minute purge. This change was made because of the depassivation of the filter observed in the earlier filter tests. In practice, the aircraft flew the LVE mission with an onboard Cl_2 passivation and calibration system. This onboard system allows the filter to be passivated with Cl_2 with the aircraft in the air, a few minutes prior to launch.

The test sequence was as follows:

- Step 1 - 5-minute passivation of aircraft sample transfer lines, HCl filter, and Cl_2 detector inlet tube at 3 ppm Cl_2 in air and at flight mission flowrates,
- Step 2 - 10-minute purge of aircraft sample transfer lines, HCl filter, and detector inlet tube with air at mission flowrates.

Step 3 - Repetitive cycles of 1-minute sample of Cl_2 -HCl-air mixture followed by 3-minute air purge at mission flow-rates.

As before, this sequence was repeated several times at two gas mixtures: mixture A - 50 ppb Cl_2 , 10 ppm HCl, balance air; mixture B - 10 ppm Cl_2 , 10 ppm HCl, balance air. New filters were used for each test sequence. Figures 12 and 13 show the Cl_2 detector response during step 3. As noted earlier, the zero cycles illustrate the output of the detector to the Cl_2 concentrations only (no HCl, no filter). For the data traces of figures 12 and 13, the data recorder was not operated for the air purge portions of step 3; therefore, the data traces in the figures are not continuous with respect to time. As indicated, the data of cycle 2 (figure 12) were recorded at a faster chart speed than the other cycles shown. As shown for the 50 ppb case (figure 12), the first cycle shows only about a 35 ppb response indicating that approximately 30 percent of Cl_2 is trapped in the HCl filter. By the fifth cycle, the output at the end of the cycle reaches 45 ppb whereas at the beginning of the cycle, was only 32 ppb. Additional cycles beyond number 5 show a similar but slightly increasing pattern of values. HCl breakthrough occurs during the 14th cycle after a HCl dosage exposure of about 8000 ppm-sec. Repetitive tests of this sequence (mixture A) indicate that at the 50 ppb Cl_2 , some Cl_2 will be lost in the HCl filter, that this amount never exceeded 30 percent, and generally was about 20 percent. The results for the 10 ppm Cl_2 - 10 ppm HCl mixture (figure 13) are similar to those of the 1.8 ppm Cl_2 filter verification tests discussed earlier in that at the 10 ppm Cl_2 concentration, only a negligible amount of Cl_2 is lost in the filter and the detector's output for cycles 1 through 19 is almost identical. HCl breakthrough did not occur through 19 cycles (11,000 ppm-sec HCl dosage). Only 19 cycles were conducted during the test.

Aircraft Sampling Procedures

Based upon the laboratory studies, the Cl_2 sampling procedures used for the August and September launch were as follows:

1. At T-1 hour (prior to aircraft takeoff), instrument zeros were set and instrument electronics gains were calibrated.
2. At T-30 minutes (aircraft is airborne by this time), instrument power was activated, sample flow rate set, and all operating parameters associated with the instrument checked.
3. At T-10 minutes, a 3 ppm Cl_2 in air mixture was generated in the aircraft sample line by mixing a predetermined amount of 300 ppm Cl_2 in N_2 (stored in a gas cylinder located in the nose of the aircraft) with the ambient air entering the sampling system of the aircraft. The Cl_2 instrument immediately began sampling this 3 ppm mixture.

4. At launch (T-zero), the aircraft was released from its prelaunch holding position and began positioning itself for the first sampling pass.
5. Thirty seconds prior to the first pass through the cloud (decision based on visual observations) the chlorine gas supply in the nose was deactivated.
6. Thirty seconds after the aircraft exited the visible cloud, the chlorine gas supply in the nose was reactivated.
7. This process of activating and deactivating the Cl_2 gas supply was performed during each sampling pass until completion of the sampling mission.
8. At the conclusion of the sampling mission and upon landing of the aircraft, instrument zeros and electronics calibration were rechecked.

As noted in the procedures, instead of initially passivating the sampling system with the onboard 3 ppm Cl_2 gas mixture and relying on the system to remain passivated for the duration of the mission, the 3 ppm Cl_2 passivation mixture is continually used to passivate the sampling system except during those brief periods when the aircraft is sampling the LVE cloud. Approximately 30 seconds prior to aircraft entry into the cloud, the 3 ppm mixture is deactivated, and 30 seconds after aircraft exit from the cloud, the mixture is reactivated. The response of the Cl_2 detector to the laboratory simulation of this procedure is shown in figure 14. The experimental apparatus is that shown in figure 11 minus the HCl gas supply. With reference to figure 14, the 3 ppm Cl_2 mixture is deactivated at 10 minutes (initially activated at time zero); approximately 30 seconds later, a 30-second dose of 0.17 ppm Cl_2 in air is introduced into the nose probe (simulates LVE cloud sampling). The 3 ppm passivation mixture from 12 to 14 minutes simulates the time between aircraft sampling passes, and introduction of the 0.17 ppm mixture at about 15 minutes simulates a second aircraft LVE cloud sampling. As shown in figure 14, the 0.17 ppm Cl_2 mixture is recorded as about 0.17 to 0.18 ppm after having corrected for Cl_2 background in the sampling system as a result of the passivation sequence. Comparison of the data of figure 14 with that of figure 8 illustrates the improvement in the magnitude of reduction of Cl_2 losses. Additional laboratory data showed the technique not to be a function of the activation and deactivation time of the 3 ppm passivation mixture in the range of 10 to 60 seconds prior to aircraft entry or after aircraft exit from the cloud. (Times outside of this range were not investigated.) The modification of the procedures had no effect on the trapping efficiency of the HCl filter.

Summary of Cl_2 Detection System Evaluation

The detection capabilities of the airborne Cl_2 detection system as determined from the laboratory studies are summarized as follows:

1. A glass wool filter is effective, up to about 10,000 ppm-sec HCl, in trapping HCl for the HCl concentration and dosages expected in the LVE cloud. When properly passivated, the filter has little effect on Cl_2 concentrations in the sample line.
2. The Cl_2 sampling system requires passivation with Cl_2 gas to prevent measurable loss of Cl_2 from the inlet sample line. A 3 ppm Cl_2 in air passivation mixture combined with the operational procedures outlined earlier are adequate to eliminate these Cl_2 losses for Cl_2 concentrations of 50 ppb to 10 ppm.
3. The detector's output is linear from about 50 ppb to about 5 ppm. Above 5 ppm, the output is non-linear. Studies below 50 ppb Cl_2 were not performed and the output is assumed to be linear with the same sensitivity as measured at 50 ppb.
4. The lower detection limit of the sampling system is below 10 ppb as calculated from signal-to-noise ratios and the measured sensitivity at 50 ppb. System accuracy for Cl_2 is about ± 20 percent reading and is controlled by the laboratory calibration uncertainties of the basic sensor.

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TABLE 1: EXHAUST PRODUCT COMPOSITION

Species	Mass Fraction in Afterburned Plume ^a (percent)	Nominal Concentration in Stabilized Ground Cloud ^b
Aluminum Oxide (Al_2O_3)	30.4	1000 - 3000 $\mu\text{g}/\text{m}^3$
Carbon Monoxide (CO)	< .1	< 1 ppm
Hydrogen Chloride (HCl)	20.4	5 - 40 ppm
Water vapor (H_2O)	31.9	-- ^c
Carbon Dioxide (CO_2)	48.0	ambient values
Chlorine (Cl_2)	2.3	-- ^d
Nitrogen Oxide (NO)	1.2	200 - 800 ppb
Others	0.6	-- ^c

^a Includes only that entrained air combusted in afterburning; total mass fraction is greater than 100 percent as reference mass for calculation is exhaust effluents from the motors.

^b Range of nominal concentrations measured in earlier Titan III monitoring programs (ref. 2-6)

^c Not measured in monitoring program

^d Not measured in previous monitoring program

TABLE II: DETECTION CAPABILITIES OF AIRBORNE
HYDROGEN CHLORIDE AND CHLORINE
INSTRUMENTS

	HCl Instrument	Cl ₂ Instrument
Range	0.5 to 200 ppm	10 ppb to 10 ppm
Response time for 90% reading	1 sec.	1 to 5 sec.
Detection limit	0.5 ppm	10 ppb
Accuracy ¹	± 10% of reading or 0.5 ppm	± 20% of reading or 10 ppb

¹Accuracy is larger of the two values.

TABLE III: AIRCRAFT SAMPLING PARAMETERS

A. August 20, 1977

Pass Number	Approximate Time (min)	Aircraft Altitude (m)
1	T + 3	760
2	T + 4	1030
3	T + 6	1220
4	T + 8	1430
5	T + 11	1310
6	T + 13	1340
7	T + 15	1340
8	T + 17	1370
9	T + 20	1220
10	T + 23	1250
11	T + 26	1070
12	T + 29	1070
13	T + 33	1000
14	T + 36	1000
15	T + 39	1000
16	T + 43	1000
17	T + 47	1000
18	T + 51	1000
19	T + 54	1000
20	T + 57	1000
21	T + 63	1000
22	T + 67	1000
23	T + 70	1000
24	T + 73	1000
25	T + 77	1000
26	T + 80	1000
27	T + 84	1000
28	T + 88	1000
29	T + 92	1060
30	T + 96	1000

TABLE III: AIRCRAFT SAMPLING PARAMETERS CONTINUED

B. September 5, 1977

Pass Number	Approximate Time (min)	Aircraft Altitude (m)
1	T + 2	670
2	T + 4	820
3	T + 6	1100
4	T + 8	1430
5	T + 12	1520
6	T + 14	1520
7	T + 17	1520
8	T + 21	1430
9	T + 25	1430
10	T + 28	1430
11	T + 30	1430
12	T + 34	1430
13	T + 37	1430
14	T + 41	1430
15	T + 44	1430
16	T + 48	1400
17	T + 52	1400
18	T + 55	1340
19	T + 58	1350
20	T + 61	1350
21	T + 65	1230
22	T + 69	1230
23	T + 72	1230
24	T + 75	1200
25	T + 88	1140
26	T + 92	1140
27	T + 95	1140
28 *	T + 98	1140
29	T + 181	1140
30	T + 189	1140

TABLE III: AIRCRAFT SAMPLING PARAMETERS CONTINUED

B. September 5, 1977

Pass Number	Approximate Time (min)	Aircraft Altitude (m)
31	T + 194	1140
32	T + 196	1140
33	T + 200	1110
34	T + 207	1140
35	T + 211	1140
36	T + 214	1140
37	T + 219	1140
38	T + 222	1170
39	T + 228	1170
40	T + 230	1170
41	T + 232	1140
42	T + 236	1140
43	T + 237	1140
44	T + 240	1140
45	T + 246	1140
46	T + 247	1140
47	T + 254	1140
48	T + 258	1100
49	T + 263	1100
50	T + 265	1160

*Landed and refueled after pass 28

TABLE IV: COMPARISON OF MAXIMUM OBSERVED
HYDROGEN CHLORIDE CONCENTRATION
WITH MAXIMUM CHLORINE CONCENTRATION

A. August 20, 1977 Launch

Pass Number	Maximum Concentration		$\frac{\text{Max Cl}_2}{\text{Max HCl}}$ $\frac{(\text{ppb})}{(\text{ppb})}$
	HCl (ppm)	Cl ₂ (ppb)	
1	26	not measured	----
2	30	42	1.4×10^{-3}
3	23	70(50)	3×10^{-3} (2×10^{-3})
4	18	82(55)	4.5×10^{-3} (3×10^{-3})
5	7	60(20)	8.5×10^{-3} (3×10^{-3})
6	7	66(35)	9.4×10^{-3} (5×10^{-3})

B. September 5, 1977 Launch

Pass Number	Maximum Concentration		$\frac{\text{Max Cl}_2}{\text{Max HCl}}$ $\frac{(\text{ppb})}{(\text{ppb})}$
	HCl (ppm)	Cl ₂ (ppb)	
1	27	40	1.5×10^{-3}
2	23	30	1.3×10^{-3}
3	12	<10	$<8 \times 10^{-4}$
4	24	22	9×10^{-4}
5	16	<10	$<6 \times 10^{-4}$
6	9.4	<10	$<1.1 \times 10^{-3}$

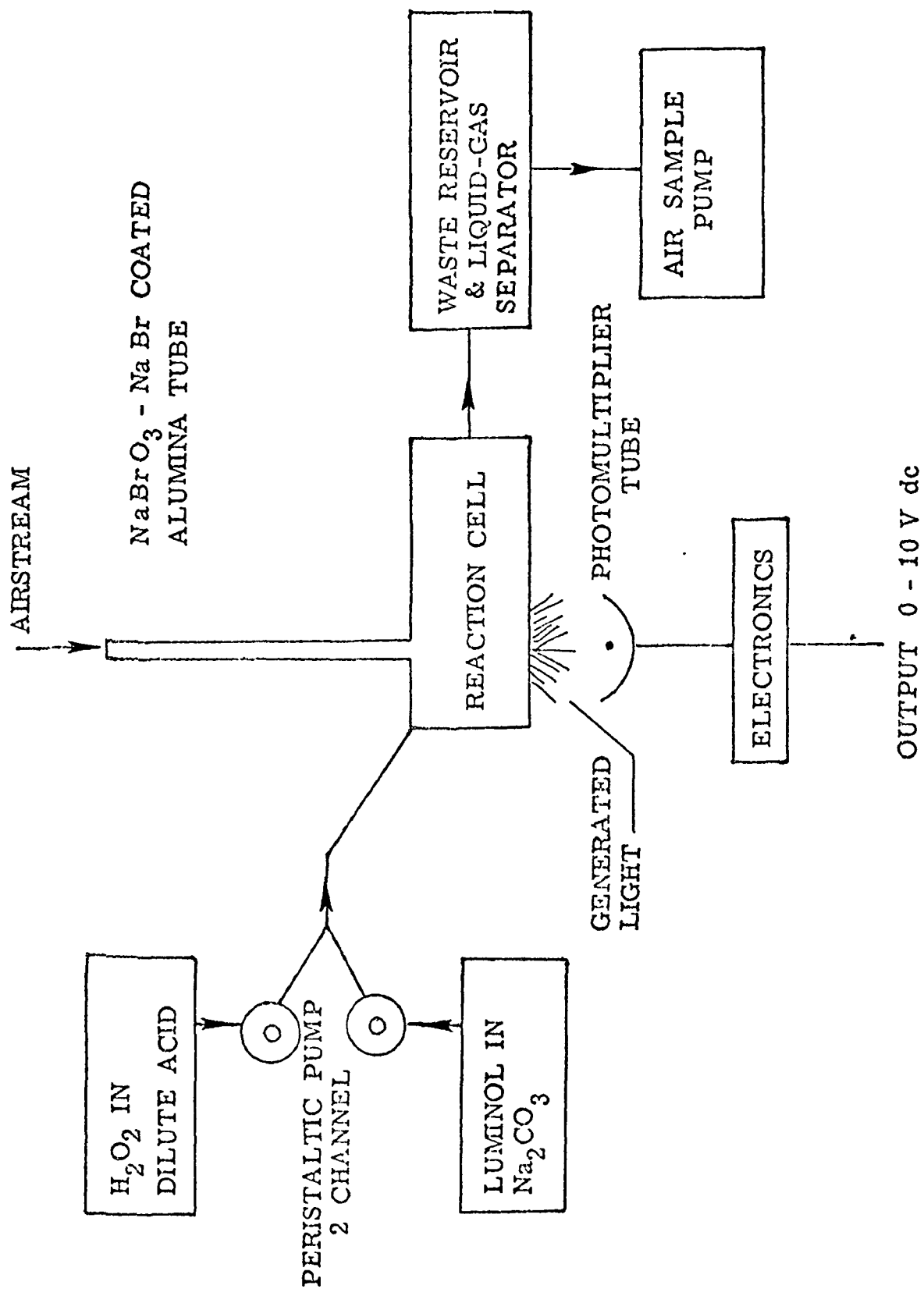


Figure 1. - Schematic of hydrogen chloride detector.

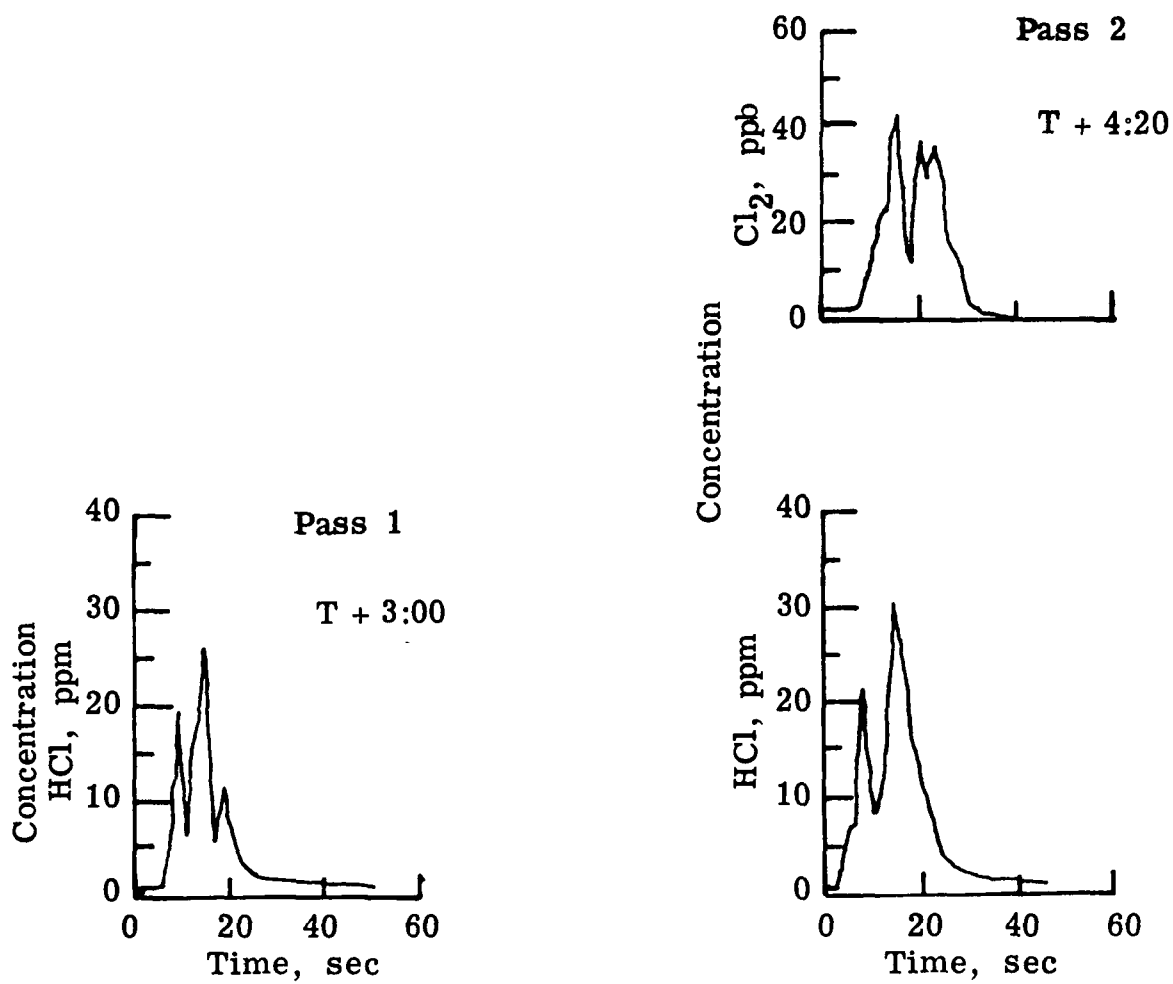


Figure 2. - Hydrogen chloride and chlorine data traces, August 20, 1977 launch.

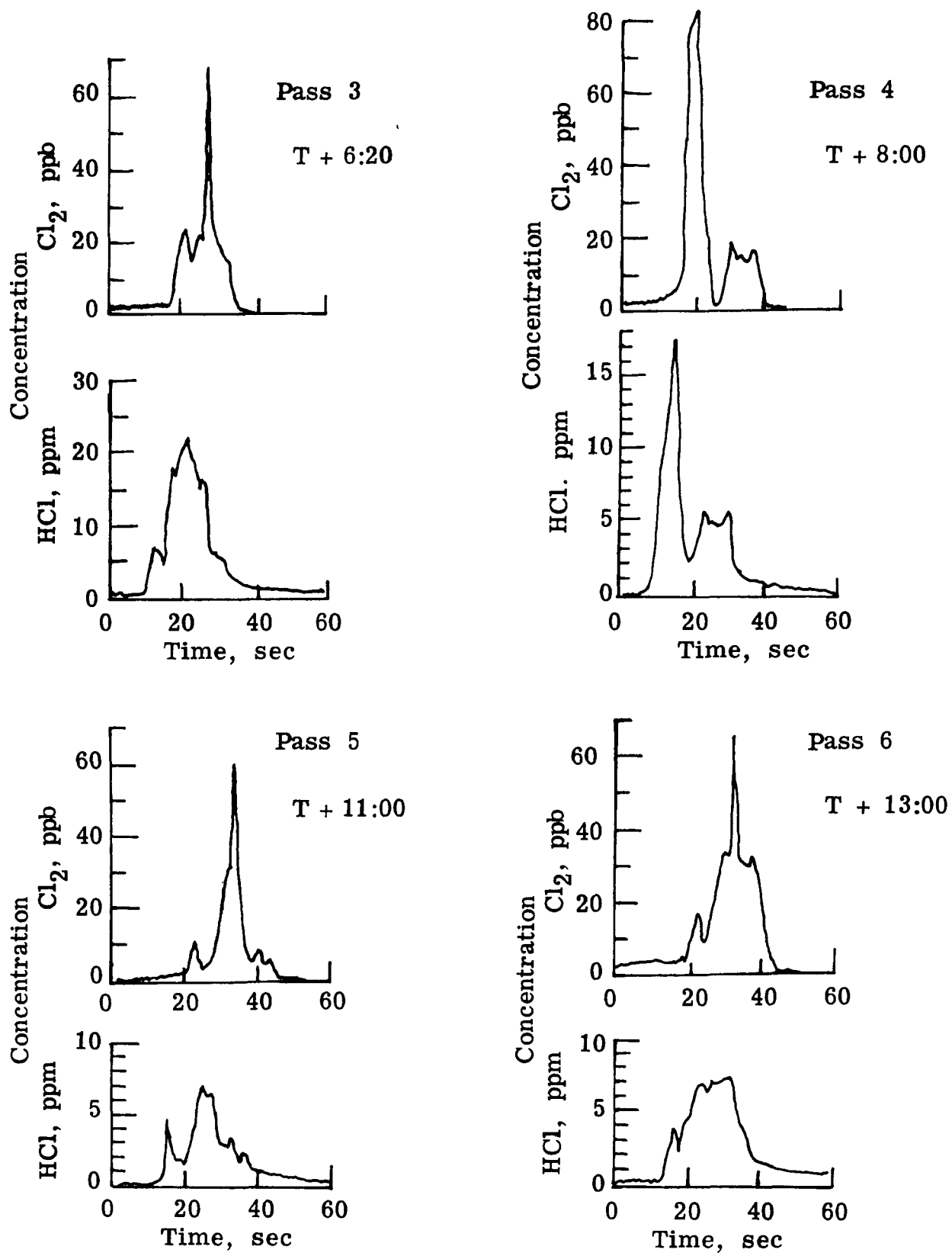


Figure 2. - concluded.

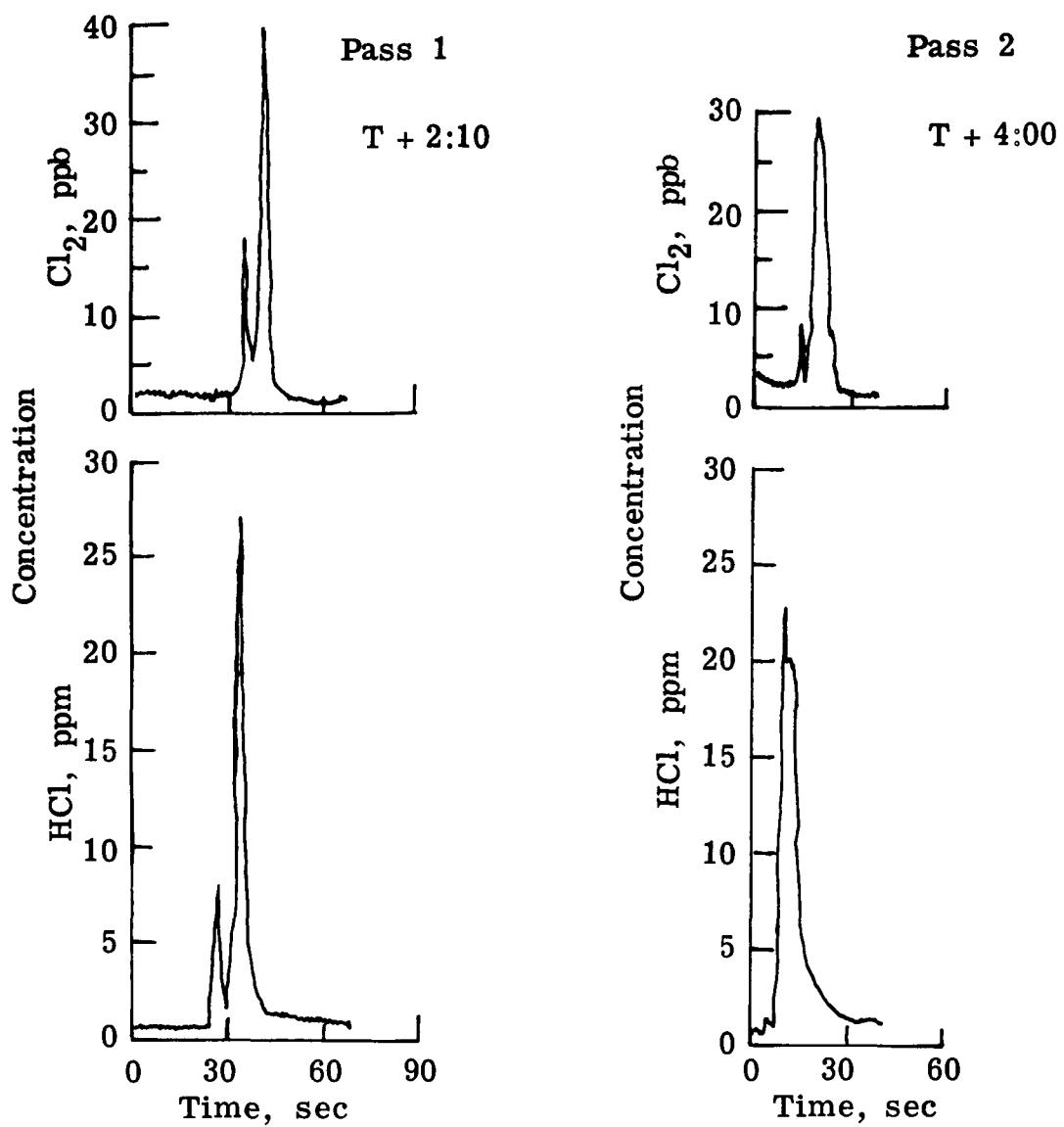


Figure 3. - Hydrogen chloride and chlorine data traces, September 5, 1977 launch.

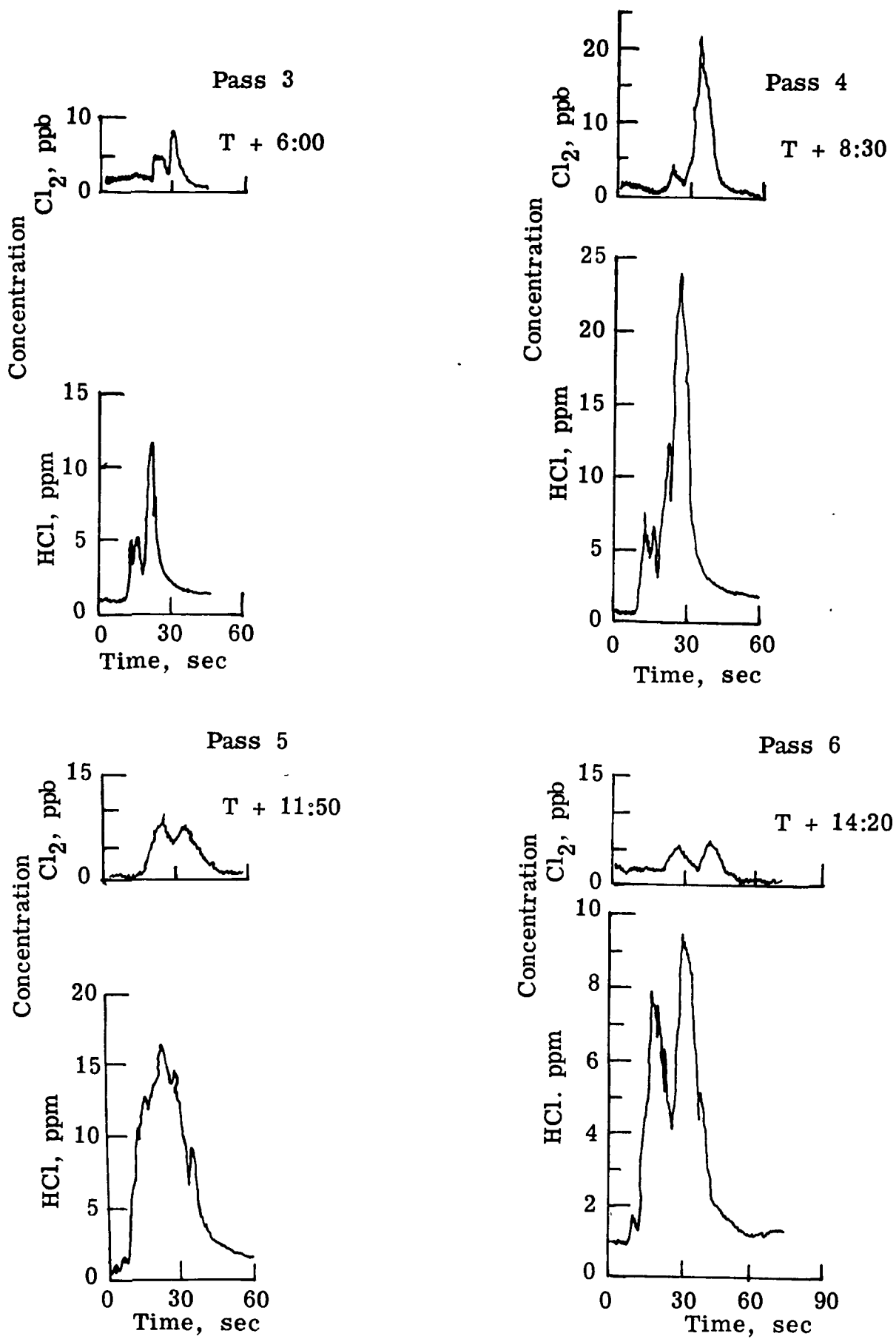


Figure 3. - concluded.

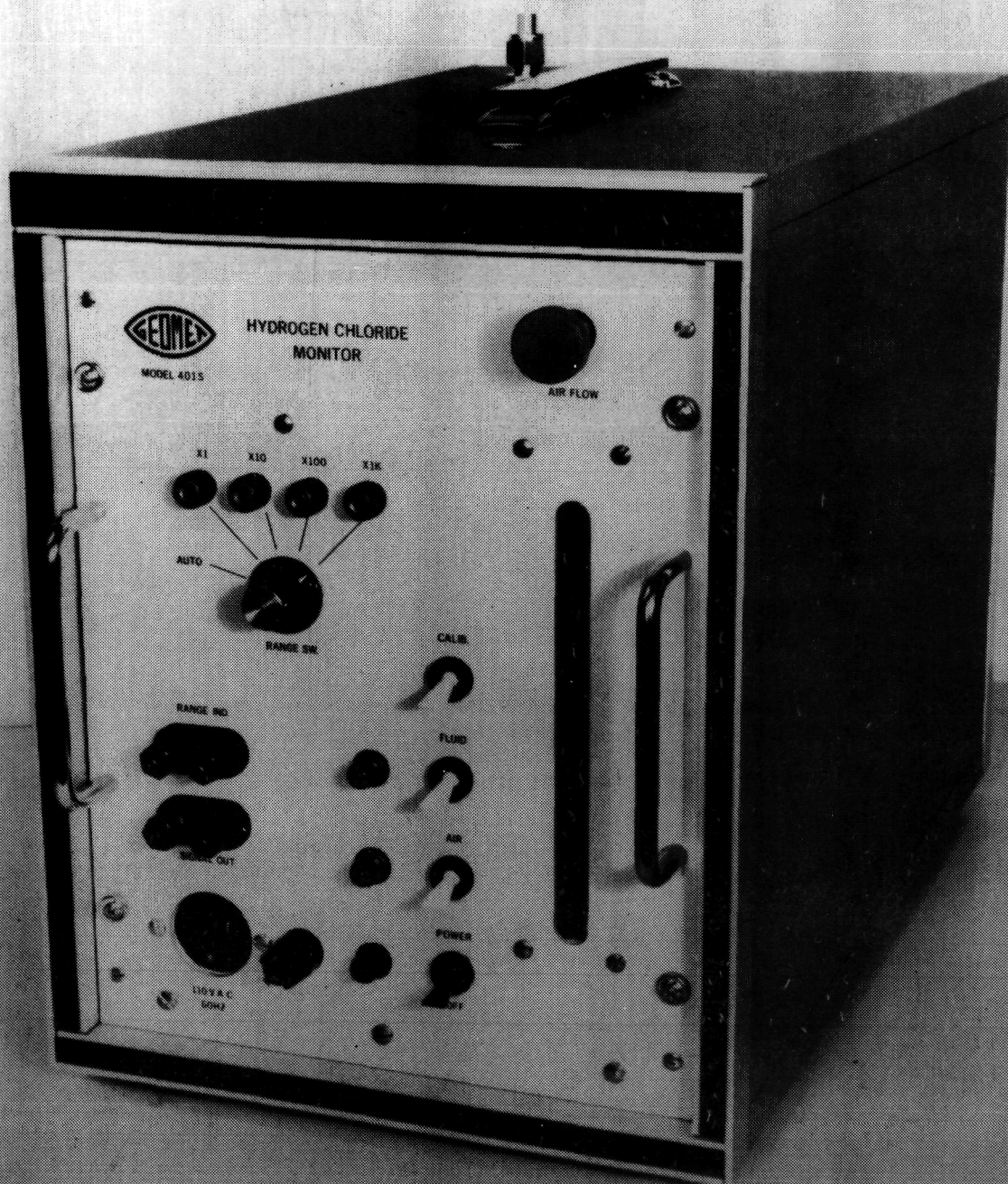


Figure 4. - Surface level hydrogen chloride detector.

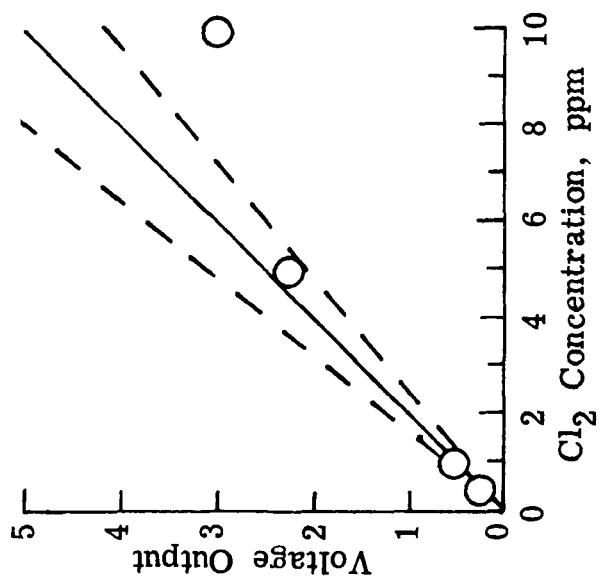
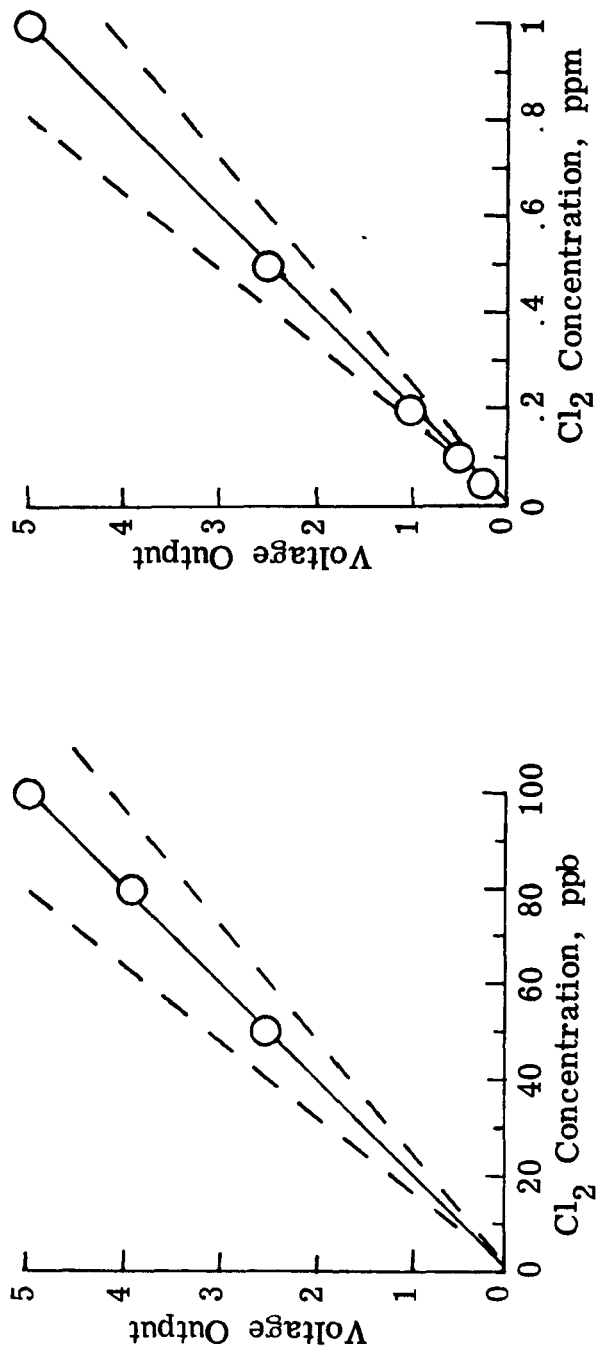
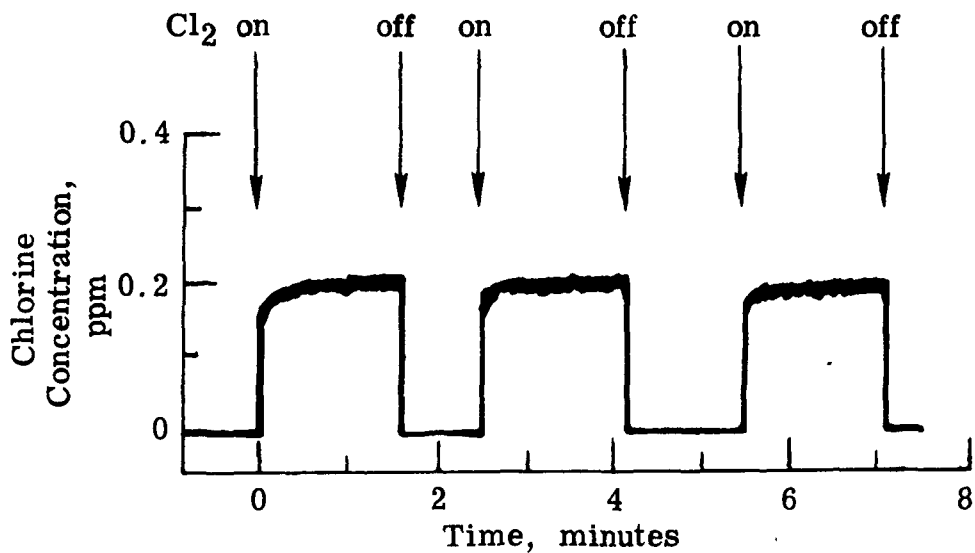
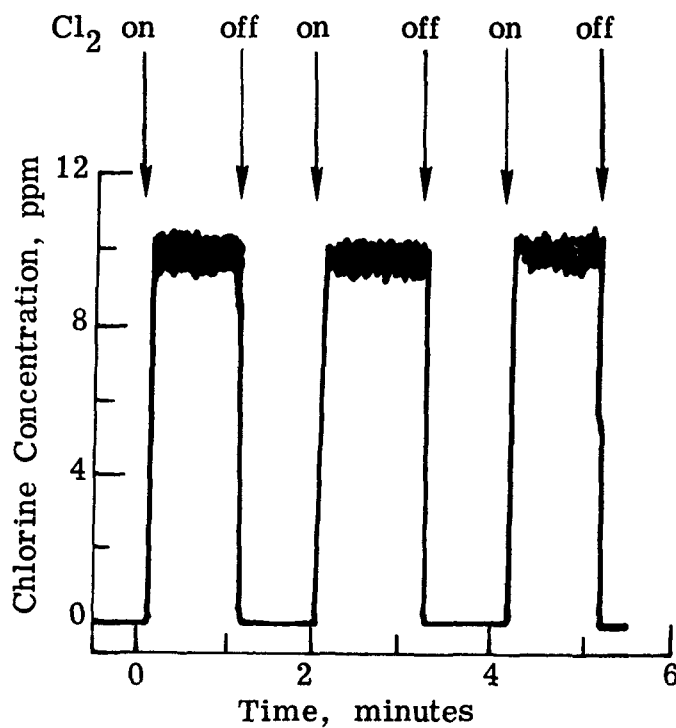


Figure 5. - Chlorine detector calibration results.



a. 0.2 ppm Cl_2 in air, $\times 100$ instrument scale.



b. 10 ppm Cl_2 in air, $\times 10$ instrument scale.

Figure 6. - Laboratory repeatability and response time results, basic chlorine detector without filter.

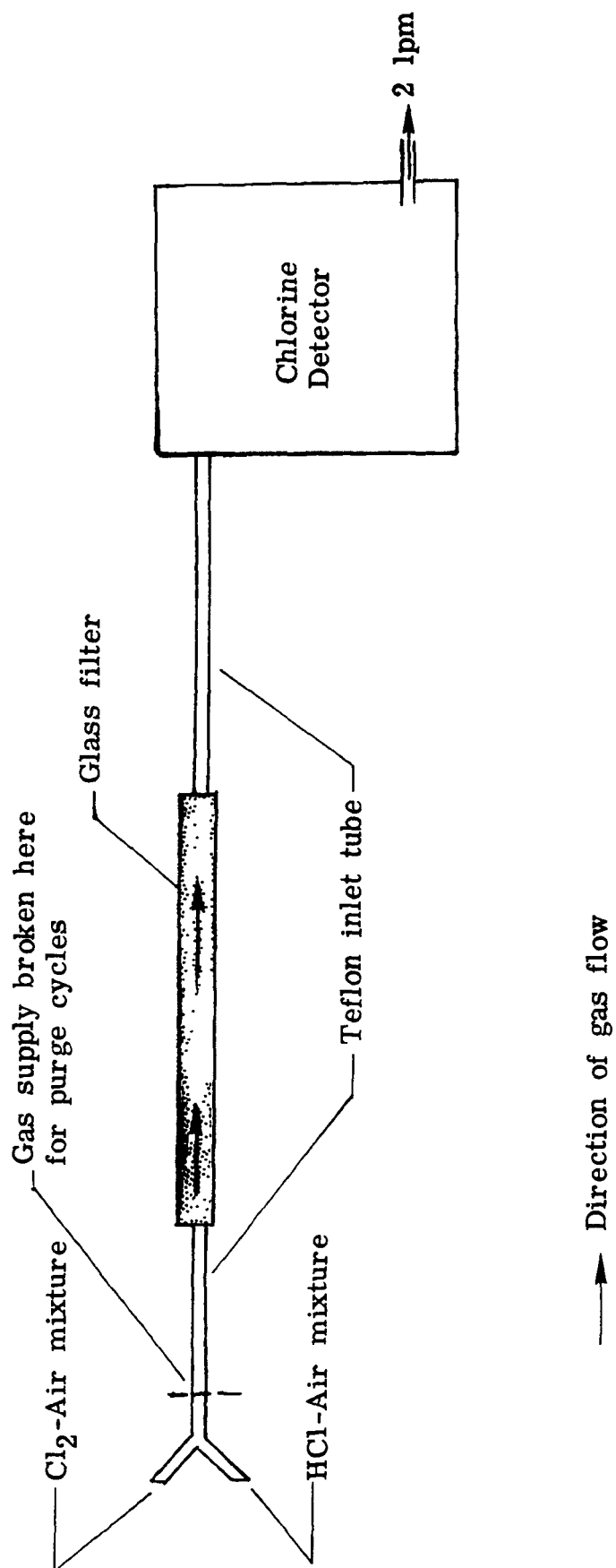


Figure 7. - Experimental setup for filter studies.

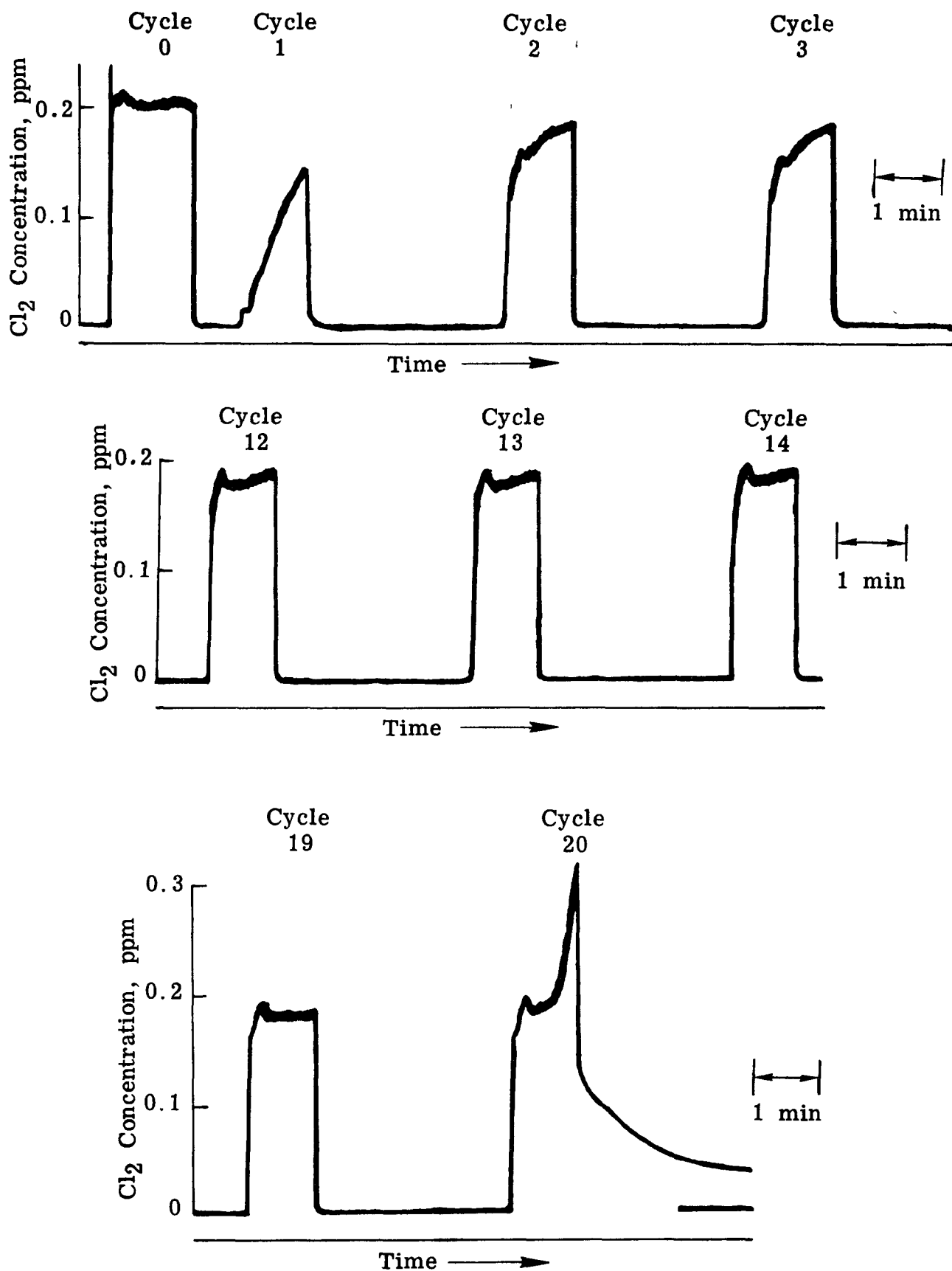


Figure 8. - Filter study results; 20 cycles of 0.2 ppm Cl_2 -10 ppm HCl-air mixture.

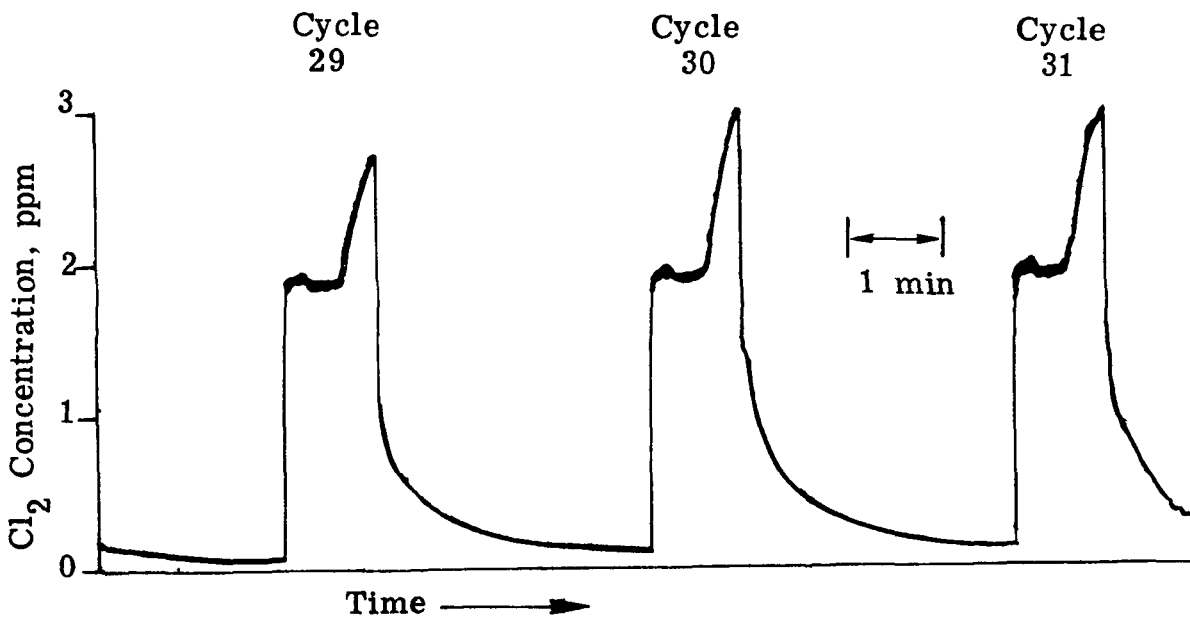
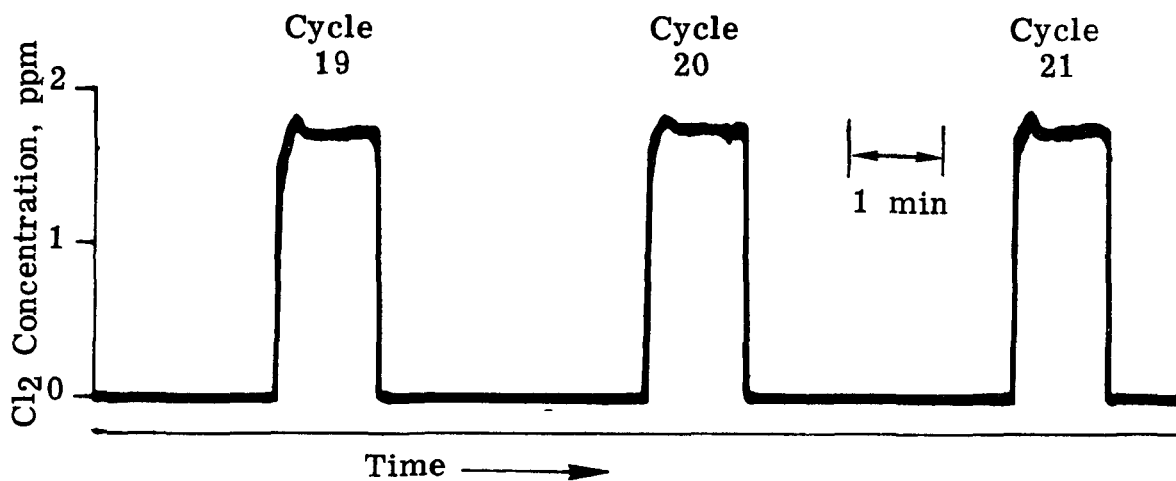
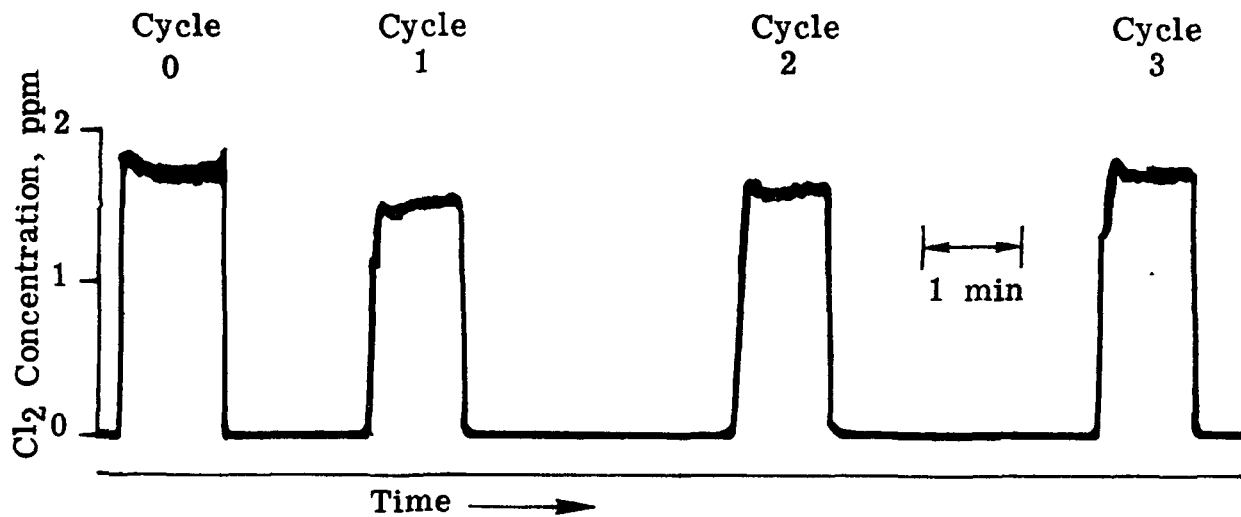


Figure 9. - Filter study results; 31 cycles of 1.8 ppm Cl_2 -10 ppm HCl-air.

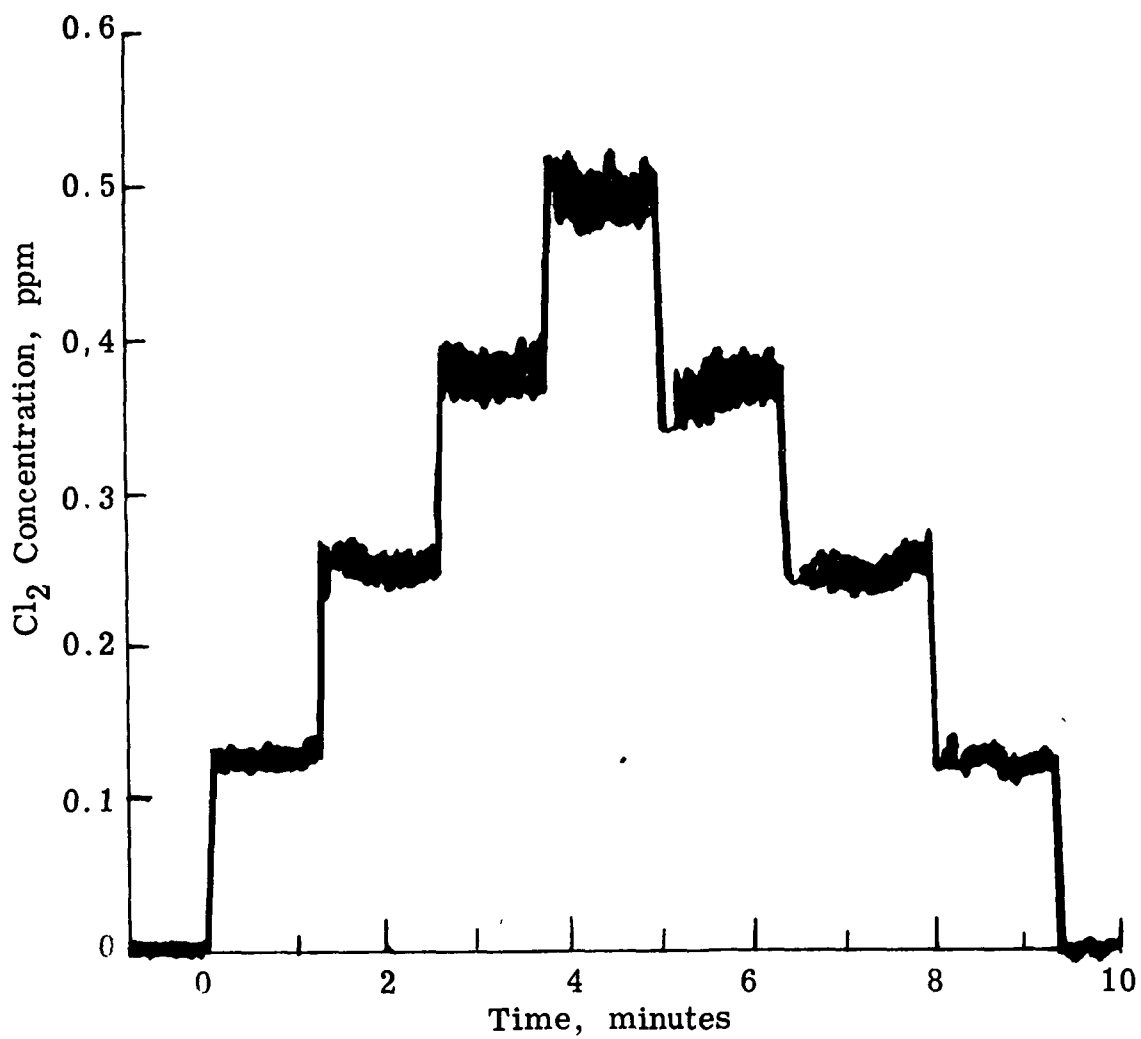


Figure 10. - Airborne system response to step changes in chlorine concentration (concentration change of approximately 0.1 - 0.15 ppm/min.)

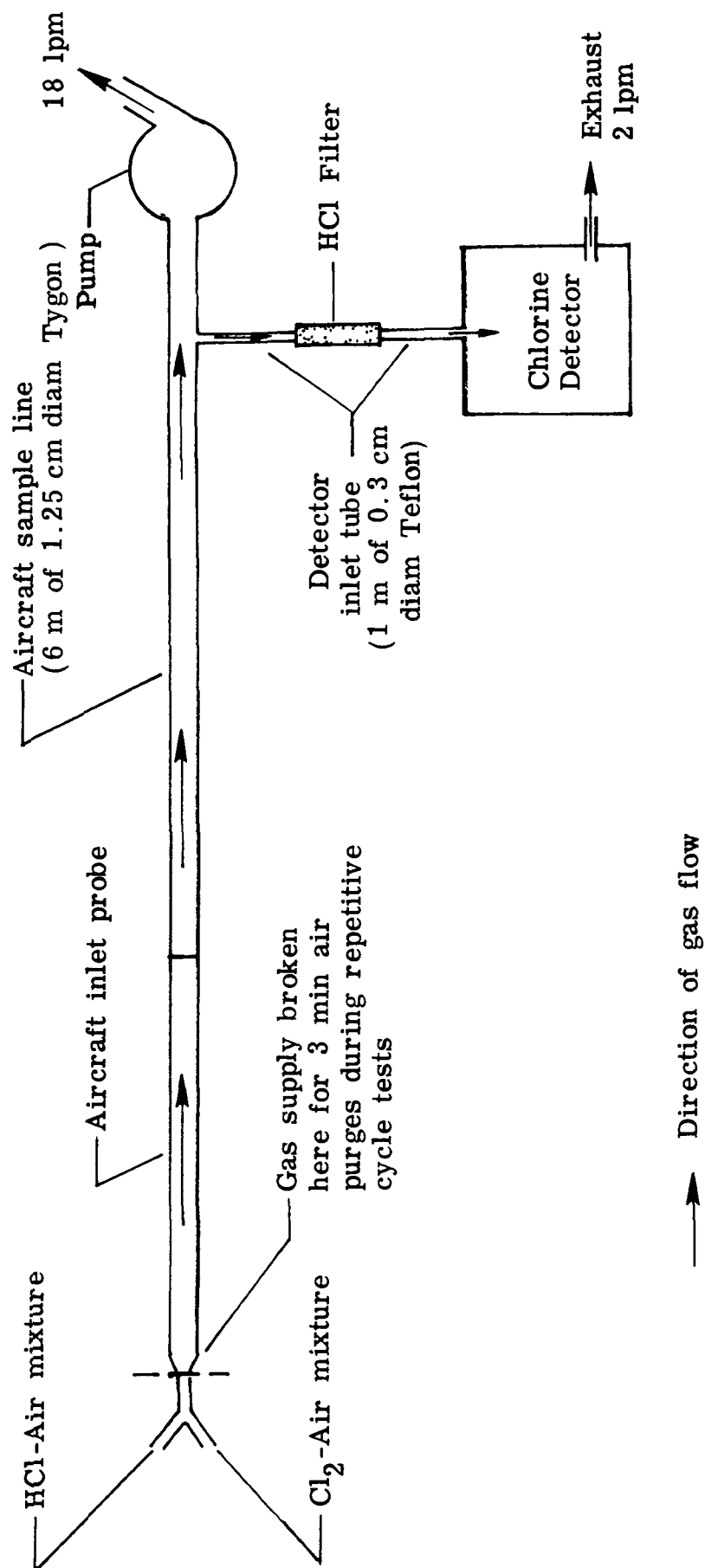


Figure 11. - Experimental setup for evaluation of airborne chlorine detection system.

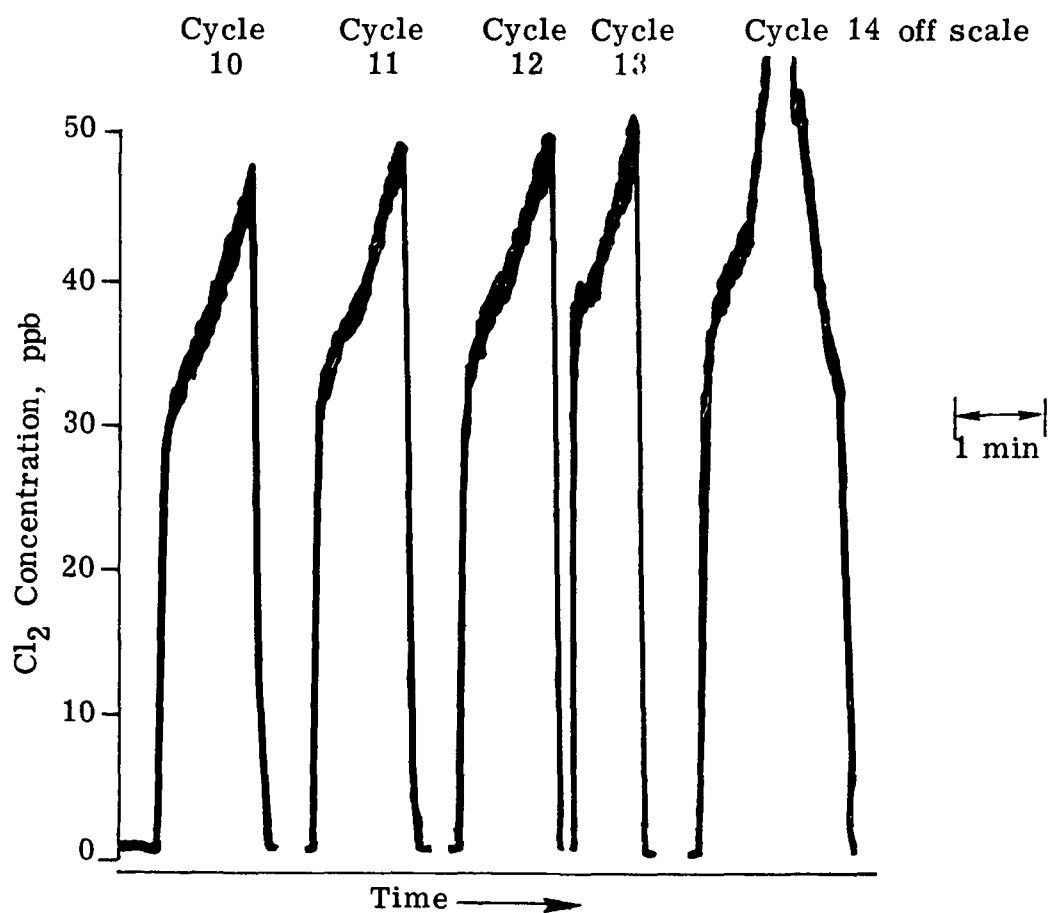
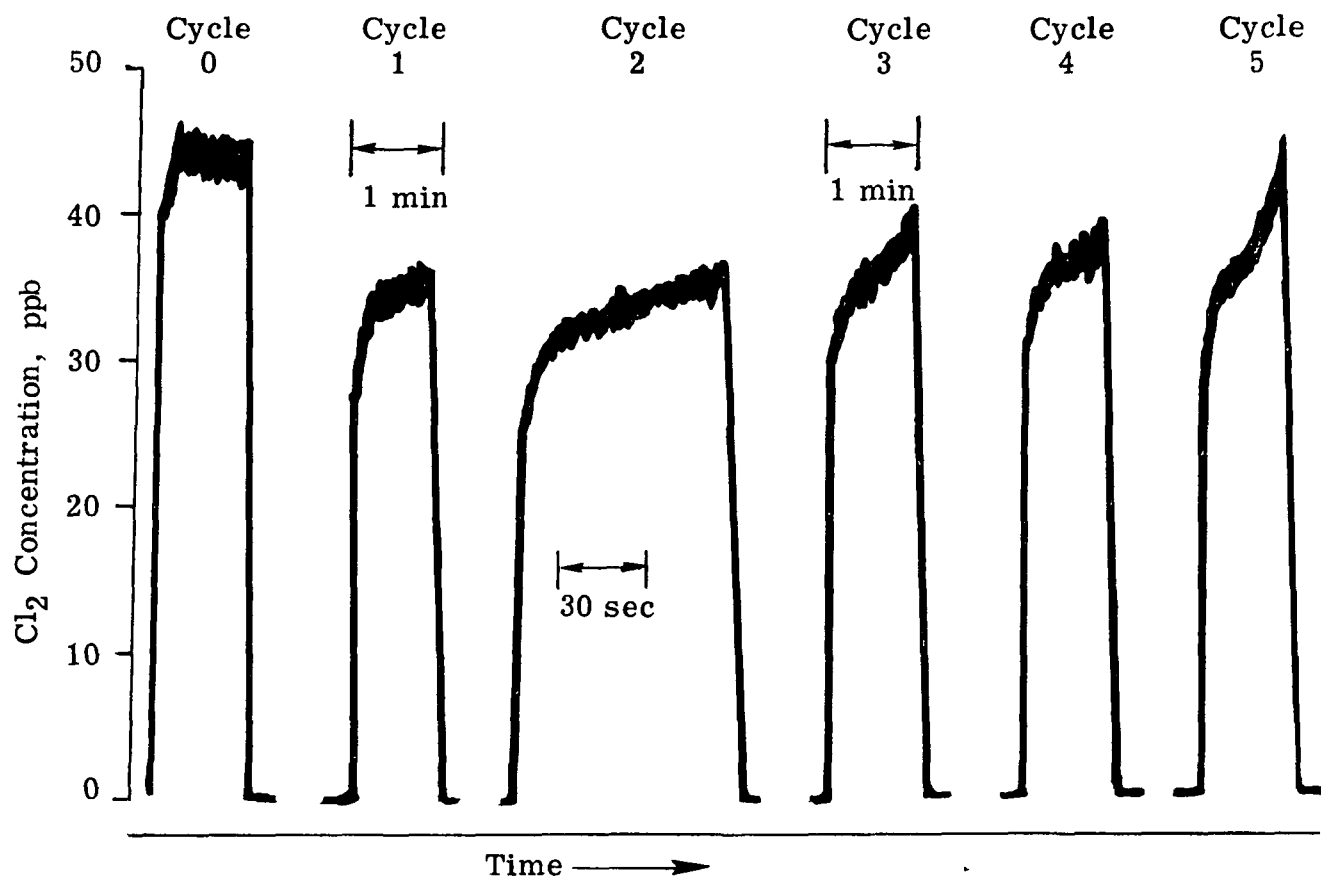


Figure 12. - Airborne sampling configuration test results;
14 cycles of 50 ppb Cl_2 - 10 ppm HCl air.

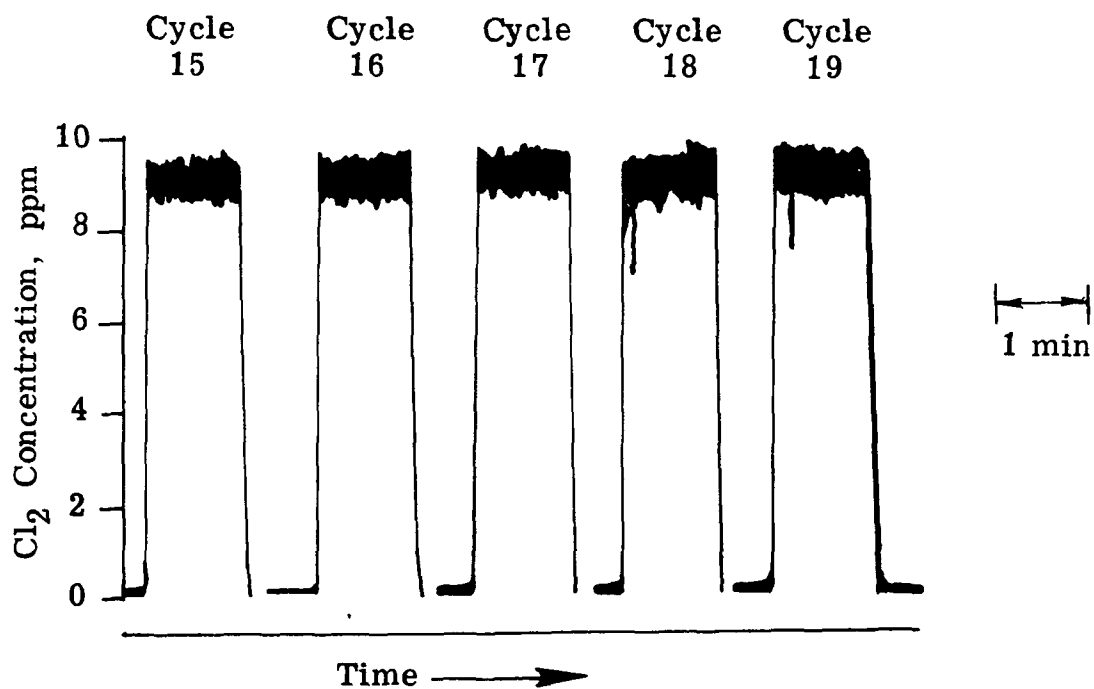
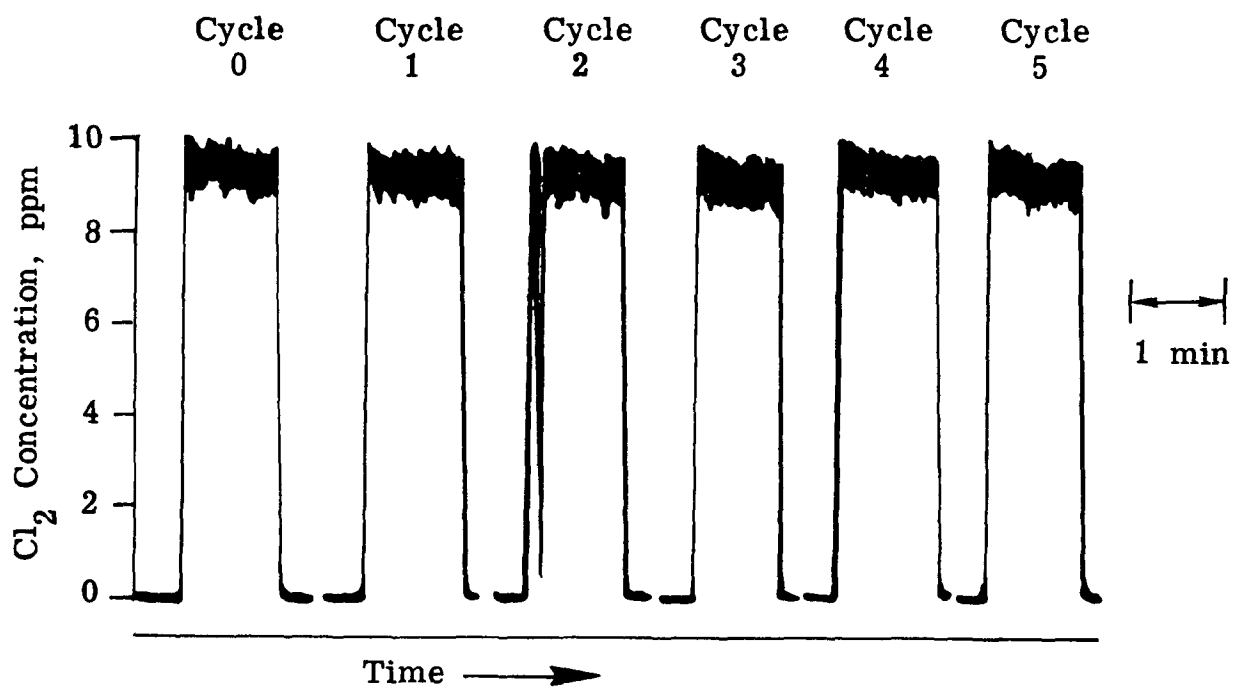


Figure 13. - Airborne sampling configuration tests results;
19 cycles of 10 ppm Cl_2 - 10 ppm HCl-air.

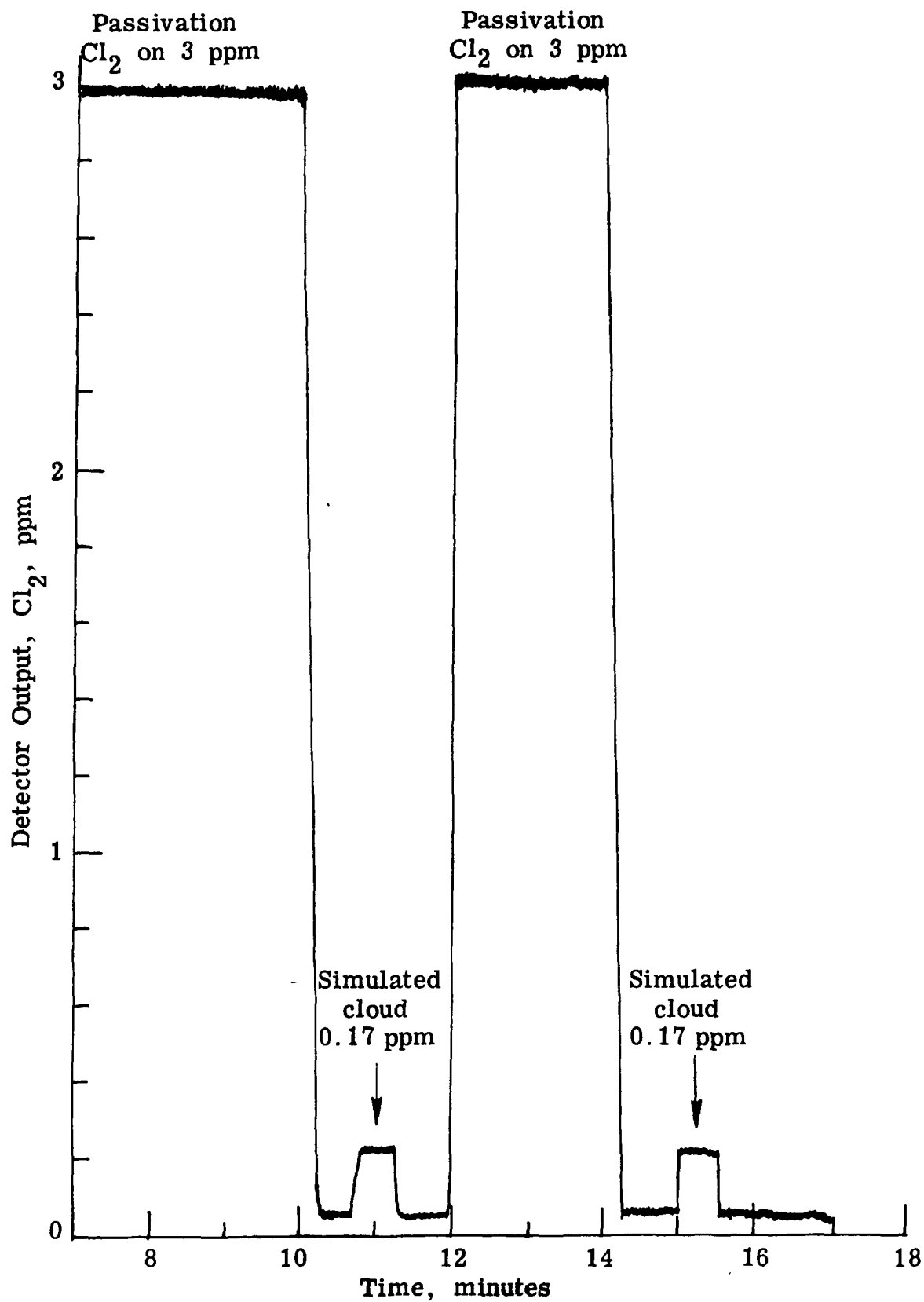


Figure 14. - Airborne sampling configuration tests results; passivated system (3 ppm Cl_2), simulated cloud of 30 second duration at 0.17 ppm Cl_2 .

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16. Abstract The report discusses airborne chlorine and hydrogen chloride measurements made in the tropospheric ground cloud following the Voyager launches of August 20 and September 5, 1977. The maximum observed hydrogen chloride concentration for both launches was about 25 to 30 parts-per-million (ppm) occurring typically 2 to 6 minutes after launch. By completion of the sampling mission (1-1/2 hours for August, 4-1/2 hours for September), the maximum in-cloud concentration decayed to about 1 to 2 ppm. Maximum observed chlorine concentrations were about 40 to 55 parts-per-billion (ppb) about 2 to 8 minutes after launch; by about 15 minutes after launch, chlorine concentrations were less than 10 ppb (detection limit). In-cloud chlorine concentrations were well below 1 percent of hydrogen chloride concentrations. The appendix of the report discusses the chlorine instrument and the laboratory evaluation of the detector.					
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